

PATENT SPECIFICATION

(11) 1 585 644

1 585 644

(21) Application No. 51708/77 (22) Filed 12 Dec. 1977 (19)
 (31) Convention Application No's 51/148980 (32) Filed 10 Dec. 1976
 51/148937 11 Dec. 1976
 51/149960 14 Dec. 1976 in
 (33) Japan (JP)
 (44) Complete Specification Published 11 Mar. 1981
 (51) INT. CL.³ C09B 5/48
 B05D 1/36
 B32B 27/30
 C08L 27/18 79/08 81/02



(52) Index at Acceptance
 C3M 105 111 159 162 171 200 201 C
 B2E 1711 407S 440T 445T 494T 494U
 495T ANA
 C3Y B140 B160 B230 B240 B243 B245
 F118 F510 F530 F583

(72) Inventors: TATSUSHIRO YOSHIMURA
 MITSUSUKE NAMBA
 SEISUKE SUZUE
 SHIGETAKE TOMINAGA
 TOSHIO MIZUMO
 NARIYOSHI HAYASHIDA

(54) FLUOROCARBON POLYMER COATING COMPOSITION

(71) We, DAIKIN KOGYO COMPANY LIMITED, A Japanese body corporate of Shin-hankyu Building, No 8, Umeda, Kita-ku, Osaka-shi, Osaka-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

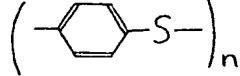
5 This invention relates to fluorocarbon polymer coating compositions. Desirable properties possessed by fluorocarbon polymers, such as low coefficient of friction, non-tackiness and high resistance to chemicals and heat, have led to the application of these polymers in a wide variety of fields such as for domestic uses (as in coating irons, 10 frying pans, etc), in the food industry, in the electric industry, in the machine industry and elsewhere. However, because of the inherent nature of non-tackiness, the fluorocarbon polymers are generally poor in adhesion to other materials. Thus, it is difficult to coat substrates with such polymers and obtain sufficient adhesion therebetween.

15 In an effort to overcome this difficulty, several methods have been proposed employing polyarylene sulphide resins (hereinafter referred to simply as PAS), typical of which is polyphenylene sulphide. (hereinafter referred to simply as PPS) on

20 account of their high resistance to heat and high affinity for fluorocarbon polymers. For example, in Japanese patent publication No 31813/1976, there is proposed a method in which a polyphenylene sulphide resin is sprayed over a blasted metal surface and baked to form, *in situ*, an undercoat layer on which a fluorocarbon polymer topcoat is to be formed. It has also been proposed, in Japanese patent publication No 12053/1976 and German 25 Offenlegungsschrift No 2.152.770, to employ primer compositions containing PPS and a fluorocarbon resin as principal components for applying a fluorocarbon polymer topcoat on the primer coat derived from the composition.

25 Neither of these proposals may be regarded as wholly satisfactory in our view. Thus, a primer coat consisting essentially of PPS has, so we find, a poor hardness at 30 elevated temperatures (e.g., a pencil hardness test result at 180 - 200°C of 2B or worse) though it exhibits good hardness at normal temperature (pencil hardness of 4H to 5H). Therefore, an article having such primer and a topcoat is liable to be scratched when hot.

35 We have found that in combinations of PPS with a fluorocarbon polymer, a satisfactory fluorocarbon polymer concentration cannot be obtained. When a composition consisting essentially of PPS admixed with a fluorocarbon polymer is used in a one-coat system, the



fluorocarbon polymer content should be in the range of up to 20% by weight. In such low content, the coat cannot exhibit good repellency properties inherent to the fluorocarbon polymer. When such composition is used as a primer composition, on the other hand, we find that sufficient adhesion between the primer coat and its fluorocarbon polymer topcoat is not obtained. To improve bonding between the primer coat and its substrate, the fluorocarbon polymer content is preferred to be as low as possible. This, in turn, is undesirable having regard to the bond between the primer coat and topcoat.

Further, when a fluorocarbon polymer admixed with PPS is used as a coating composition for a one-coat system, we have found that the resulting coat tends to lose its lubricity within a short period of service because of its poor abrasion resistance.

In accordance with the present invention, we provide a coating composition comprising a polyarylene sulphide resin, a fluorocarbon polymer and at least one imido-containing resin selected from polyamideimide resins and polyimide resins.

Suitable such compositions having a relatively small fluorocarbon polymer content have been found useful as primer compositions, while certain such compositions having a relatively large polymer content may be used in a one-coat system.

The invention further extends to articles coated with an above-described coating composition.

Other features and advantages of the invention will become apparent from the detailed description of the invention by way of example, which follows.

Polyarylene sulphide resins (PAS) are polymers having the recurring unit of an aryl group and sulphur or recurring unit composed of an aryl group and a group containing sulphur and oxygen. These polyarylene sulphide resins are particularly described in United States Patent No. 3,354,129, the disclosure of which is hereby incorporated by reference.

Both polyamideimide resins (hereinafter referred to simply as PAI) and polyimide resins (hereinafter referred to simply as PI) are polymers having relatively high resistance to heat. PAI is characterized by having both an amido radical and an imido radical in a molecule thereof, and can be prepared, for example, by interaction of an aromatic diamine having an amido radical in the molecule thereof and an aromatic tetravalent carboxylic acid such as pyromellitic acid, by interaction of an aromatic trivalent carboxylic acid such as trimellitic anhydride and a diamine such as 4,4'-diaminodiphenyl ether, and by interaction of a dibasic acid having an aromatic imido ring in the molecule thereof and a diamine. PI is a high molecular weight polymer having imido linkages in the molecule thereof and obtained by interaction, for example, of an aromatic tetravalent carboxylic anhydride such as pyromellitic anhydride and an aromatic diamine such as diaminodiphenyl ether. Any known PAI and PI can be suitably used.

Illustrative of the fluorocarbon polymers we have found useful in the practice of the present invention are polytetrafluoroethylene; copolymers of tetrafluoroethylene and hexafluoropropylene, chlorotrifluoroethylene, perfluoroalkyltrifluorovinyl ether (R_1OCFCF_3) and the like; polychlorotrifluoroethylene and mixtures thereof. The fluorocarbon polymers may be used in any form such as powder, an aqueous dispersion obtained by an emulsion polymerization, a dispersion obtained by dispersing fluorocarbon polymer powders in an aqueous medium, an organosol of fluorocarbon polymers, or an organosol-in-water emulsion.

The three components of our compositions are suitably blended in the form of a dispersion in a liquid carrier.

Because the presence of PAI and/or PI in the composition makes it possible to increase the concentration of fluorocarbon polymer, the composition may exhibit the excellent properties inherent to the fluorocarbon polymer and, therefore, may be used as a single coat in a one-coat system which requires no further coat thereover, as well as a primer coat. Further, in specific examples the coat obtained has been found to show an excellent abrasion resistance and high hardness at high temperatures.

It is preferred that the weight ratio of PAI and/or PI to PAS be in the range of 5/1 to 1/50, are more preferably in the range of 3/1 to 1/40. An excess PAI and/or PI content will lower the corrosion resistance of the composition, while too small a content will produce a coat having lower hardness at high temperatures.

The ratio by weight of fluorocarbon polymer to the total of PAS and PAI and/or PI is widely variable, but preferably in the range of 5/1 to 1/1 in the case of one-coat system and 3/1 to 1/3 in the case of a primer coat.

To improve adhesion between a topcoat and a primer coat, it would be desirable to increase the fluorocarbon polymer content in the primer composition. However, excess fluorocarbon concentration will, in turn, result in insufficient adhesion between the primer coat and its substrate. Thus, proper selection of the fluorocarbon polymer content should be made according to the type of coated article to be produced. For a one-coat system, too, the fluorocarbon polymer content should be chosen with due consideration of the adhesion

between the substrate and the one-coat, and the abrasion resistance and hardness of the one-coat.

The coating composition may include various conventionally used additives. Typical additive is a surface active agent which serves to improve the stability of the dispersion of the resin components and additives, and the levelling effect of the coat.

Illustrative of the surface active agents are anionic surface active agents such as fatty acids, sulphuric acid esters of higher alcohols, alkylbenzenesulphonic acids, alkynaphthalene sulphonic acids, polynaphthalenesulphonic acid, dialkylsulphosuccinic acids and their salts, alkylphosphoric acids and their salts, fluoroalkyl-containing carboxylic, sulphonic and phosphoric acids and their salts or esters; non-ionic surface active agents such as polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene acryl ethers, sorbitan fatty acid esters, polyoxyethylenepolyoxypropylene condensation products, etc. These surface active agents may be employed singly or in combination.

As another additive, the coating composition may contain a pigment which is stable under baking conditions of the coat, e.g. oxides of titanium and iron, carbon powder.

To the coating composition may further be added a viscosity controlling agent; a binder such as methylcellulose, ethylcellulose, poly(α -mesitylene), an oil or wax of a chlorotetrafluoroethylene telomer, a fluorinated polyether, talc, mica; a levelling agent such as a fluoroalkylcarboxylic acid, a sulphonic acid salt; a film hardner such as a metal particulate, silica, a silane coupling agent, ceramic powder; and a wetting agent such as organic solvents, for example, polyhydroxy alcohols and their esters.

The coating composition is prepared by homogeneously dispersing or dissolving the above-described three kinds of resins and, if desired the above-described additives in a liquid carrier, preparation methods of which would be within the level of ordinary skill.

PPS which is generally available as powder, is preferably finely pulverized so as to produce a homogeneous dispersion. PAI and PI are available as powder, organic solutions or dispersions, any of which is suitably employed as it is, in the preparation of the coating compositions. It will be noted that in order to ensure formation of a uniform film of the resin composition, it is preferred that the liquid carrier comprise a solvent capable of dissolving the PAI and/or PI at least under film-forming conditions, i.e. a solvent capable of dissolving PAI and/or PI at normal temperature or up to its boiling point. Examples of such solvents include N-methylpyrrolidone, cresol, phenol, naptha, dimethylformamide, dimethylacetamide, benzonitrile, methylglycol acetate, methyl ethyl ketone, 2-nitropropane, ethylglycol acetate, ethyl acetate, xylene, toluene, methyl-isobutyl ketone, and mixtures thereof including, for example, mixtures of N-methylpyrrolidone and toluene, ethyl acetate, butyl glycol, dioxane, etc.

Fluorocarbon polymers are generally available as powder, aqueous dispersions or organosols, any of which is suited for the preparation of the coating compositions.

When a fluorocarbon polymer in the form of an aqueous dispersion or its concentrated form is used which is obtained by emulsion polymerization, PAS and PAI and/or PI are first dispersed in water with the use of a surface active agent, to which the fluorocarbon polymer-containing dispersion is subsequently added, thereby to produce a coating composition in the form of an aqueous dispersion.

In the case of a fluorocarbon polymer in the form of powder, it is admixed with PAS and PAI and/or PI in water or an organic carrier. In this case, when the PAI and/or PI are in the form of powder, it is necessary to add to the mixture the above-described solvent capable of dissolving the PAI and PI. Moreover, when water is used as the carrier, a surface active agent is preferably added to the mixture. In case where organic carrier is used, all the components except the fluorocarbon polymer may be first dispersed in the carrier, to which the fluorocarbon polymer is mixed.

In the case of fluorocarbon polymer in the form of organosols, it is preferably mixed after or simultaneous with the mixing of PAS and PAI and/or PI in an organic carrier. In this case, it is preferred that the organic carrier be the same as the organic liquid contained in the organosols, though it is not essential.

The coating composition can be applied to the substrate, generally a metal substrate in any of the conventional ways such as spraying, dipping, flow coating and the like. The applied composition is then dried and baked in any suitable ways at a temperature sufficient to fuse the PAS in the dried coat, generally at about 270 - 420°C.

For example, when polytetrafluoroethylene or a copolymer containing mainly tetrafluoroethylene is used, the baking is performed at a temperature of 340 - 400°C. When the coating composition is employed as a primer coat, coating of a topcoat is also conducted in any known way.

Disadvantages involved in the prior proposals in which PAS is used as a primer for coating a fluorocarbon polymer or in which a fluorocarbon polymer is admixed with PAS is used as a primer for a fluorocarbon topcoat or as a coat in a one-coat system, are now

overcome by the provision of specific embodiments of coating composition in accordance with the present invention. By the use of PAS in conjunction with PAI and/or PI, the coat derived from the coating composition can exhibit excellent hardness at usual cookware heating temperature, i.e. around 200°C. Further, the baking temperature of the coating composition can be increased to 370 to 390°C, at which temperature excellent adhesion between the coat and its substrate is established.

The following non-limiting examples will further illustrate the present invention, in which parts and percentages are by weight unless otherwise defined.

10 *Example 1*

1st Component PPS powder (sold by Phillips Petroleum Company, U.S.A. under trademark of "Ryton V-1"), finely pulverized to have mean particle size of 10 μ

15 2nd Component PAI aqueous dispersion obtained by mixing and pulverizing, by means of a colloid mill, 700 parts of PAI (sold by Rhone-Poulenc, France, under trademark of "Rhodeftal R-200" and being a N-methylpyrrolidone solution containing 30% resin component) and 300 parts of water deionized by an ion exchanger

20 3rd Component Aqueous dispersion containing 60% polytetrafluoroethylene polymer

25 4th Component Aqueous dispersion of titanium oxide, obtained by mixing and pulverizing 60 parts of titanium oxide, 120 parts of deionized water and 30 parts of sodium lauryl sulphate by a ball mill

30 5th Component 2% carboxymethylcellulose solution

35 Using the components as set forth above, eight coating compositions having different formulations as indicated in Table 1 were prepared by mixing with a high speed mixer for about 1 hour. Each of the compositions was applied, by spraying, onto an aluminium plate with sand-blasted surface, so as to give a film having a thickness, after baking, of 20 to 25 μ . Each of the plates was then dried and baked at 370°C in an electric oven for 20 minutes. After cooling at room temperature, each coated plate was subjected to the following tests. The test results were as summarized in Table 1.

40 Pencil hardness test: in accordance with Japanese Industrial Standard K-6894

45 Brine spray test: in accordance with Japanese Industrial Standard Z-2371

50 Repellency test: 0.04 % aqueous perfluorooctanoic acid ammonium salt solution and n-hexadecane were each applied by one drop, by means of an injection spring, on a horizontally placed coated plate. The plate was then slanted at 45 degree to observe the manner of the flow of the solution and n-hexadecane on the plate and the flow traces thereof left on the plate. On the basis of the observation, the repellency property of the plate was determined.

55 *Example 2*

1st Component PPS powder (same sample as used in Example 1)

2nd Component PAI solution (same 30% N-methylpyrrolidone solution as used in Example 1)

3rd Component Polytetrafluoroethylene organosol (manufactured by Daikin Kogyo Co., Ltd., Japan)

40 4th Component Titanium oxide pigment (manufactured by Ishihara Sangyo Kaisha Ltd., Japan)

45 Using the above-mentioned components, seven dispersions having different formulations as shown in Table 2 were prepared by mixing with a high speed mixer. To each of the dispersions was added an aromatic organic solvent so as to have the viscosity of 200 to 400

5

10

15

20

25

30

35

40

45

50

55

60

65

cp, whereby to obtain coating compositions. In the same manner as described in Example 1, aluminium plates coated with each composition were produced, which were then subjected to the tests described in Example 1. In this Example, the following test was additionally conducted. The test results are shown in Table 2.

5 Taber abrasion test: Taber abrasion test machine (manufactured by Taber Instrument Co., U.S.A.) was used. The test was conducted with abrasion ring of cs-17 and a load of 750 g. After 1000 times rotation, test sample was weighed to calculate the decrease in the weight. When the decrease by abrasion is below 40 mg in amount, the test sample is determined as having good abrasion resistance. When the decrease not lower than 40 mg, 10 the test sample is regarded as having poor abrasion resistance.

5

10

Example 3

15 In this example, the same components as used in Example 2 were employed except for the 3rd component; the 3rd component being replaced with finely divided tetrafluoroethylene/hexafluoropropylene copolymer having a mean particle size of 50 μ (manufactured by Daikin Kogyo Co., Ltd., trademark "Neoflon N-20"). Using these components, four dispersions having different formulations as shown in Table 3 were prepared in the same manner as in Example 2. After controlling the viscosity in the same manner as in Example 2, the dispersions were, also in the same manner as in Example 2, 20 each applied to aluminium plates and, then, baked. The characteristics of the thus obtained coated aluminium plates were as shown in Table 3.

20

Example 4

25 In this example, the coating compositions Nos. 3, 4, 6 and 7 of Example 1 were used as primer compositions and coated on iron plates. Prior to coating, the iron plates were subjected to sand blast treatments (Emery 100). Each of the coating compositions was sprayed on the plate, dried and baked, thereby giving iron plates each having a primer coat of 10 - 13 μ thickness. The thus primed plates were, then, overlaid with a topcoat as follows. 30 A polytetrafluoroethylene topcoat composition (manufactured by Daikin Kogyo Co., Ltd., trademark "Polyflon EK 4108 GY, solid content 41%") was sprayed on each of the primed plates to give a topcoat film of 15 - 20 μ thick. The plates were then, as in the primer coating, dried, baked and cooled to give four kinds of coated plates. These plates were subjected to a series of tests, giving the results as shown in Table 4. Adhesion strength was determined as follows:

30

35 The topcoating with the Polyflon EK 4108 GY was repeated 7 times in total. Two parallel incisions were given to the coat by a knife with an interval of 10 mm. Attaching one end of the incised portion to a universal testing machine, that portion was peeled off from the iron plate while measuring adhesion strength.

35

40 *Example 5*

40

1st Component PPS (same sample as used in Example 1)

45 2nd Component PAI (same sample as used in Example 1)

45

3rd Components Polytetrafluoroethylene aqueous dispersion (resin content 60%)

40 4th Component Aqueous iron oxide dispersion obtained by mixing and pulverizing 30 parts of a red iron oxide pigment (manufactured by Titan Kogyo Company, Japan), 10 parts of a surface active agent (manufactured by Rohm and Haas Co., U.S.A., Trademark "Triton X-100") and 100 parts of deionized water, with the use of a colloid mill.

50

55 5th Component 3% aqueous methylcellulose solution

55

60 10 parts of the 1st component, 10 parts of the 2nd components, 20 parts of the 3rd, 5 parts of the 4th and 55 parts of the 5th component were blended to give an aqueous coating composition. An aluminium plate was primed with the coating composition in the same manner as in Example 4. Topcoating was performed in the same manner and with the use of the same topcoat composition as in Example 4. The pencil hardness, brine spray test and Taber abrasion test revealed that the coated plate had similar properties to those of Example 4. Adhesion strength was found to be 2.5 Kg/cm.

60

65 *Example 6*
65 Using the same components as used in Example 1 except for the 2nd component, five

65

coating compositions having different formulations as shown in Table 5 were prepared in the same manner as in Example 1. As the 2nd component, an aqueous PI dispersion was employed which had been prepared by mixing and pulverizing 350 parts of a PI solution (sold by Rhone-Poulenc under the registered trademark of "Nolimide 605" and being a N-methylpyrrolidone solution containing 60% of resin content) and 300 parts of deionized water by means of a colloid mill.

Each of the coating compositions was applied to an aluminium plate, dried and baked in the same manner as in Example 1. A series of the tests gave the results shown in Table 5.

TABLE 1

Composition No.	PPS/TiO ₂	Weight ratio PPS/PAI	PPS+PAI/PTFE	Properties of coat		Repellency
				Room Temp.	200°C	
1	100/5	20/1	1/5	H	F	no blister
2	100/5	20/1	1/3	H	F	no blister
3	100/5	20/1	1/2	2H	F	no blister
4	100/5	20/1	1/1	3H	F	no blister
5	100/5	20/1	2/1	3H	H	no blister
6	100/5	100/0	1/2	HB	2B>	no blister
7	100/5	0/100	1/2	5H	3H	blistered
8	100/5	20/1	100/0	5H	2H	no blister
						very good
						very good
						poor

Comparative
Example
Example

Composition No.	PPS/TiO ₂	PPS/PAI	PPS+PAI/ FR	Properties of coat				
				Weight ratio	Pencil hardness Room temp.	200°C Brine spray test result (200 hrs)	Repellency	Abrasion resis- tance
1	100/5	5/1	1/5	H	F	no blister	very good	good
2	100/5	5/1	1/3	H	F	no blister	very good	good
3	100/5	5/1	1/2	2H	H	no blister	very good	good
4	100/5	40/1	1/1	3H	F	no blister	very good	good
5	100/5	40/1	2/1	3H	H	no blister	good	slightly poor
6	100/5	40/1	3/1	3H	H	no blister	good	slightly poor
7	100/5	100/0	1/2	F	2B>	no blister	very good	poor

TABLE 2

TABLE 3

Composition No.	PPS/TiO ₂	Weight ratio	Properties of coat					
			PPS/PAI FR	PPS+PAI/ FR	Pencil hardness Room temp.	200°C	Brine spray test result (200 hrs)	Repellency
1	100/15	15/1	1/5	H	HB	no blister	very good	good
2	100/15	15/1	1/3	H	F	no blister	very good	good
3	100/15	15/1	1/2	3H	H	no blister	very good	good
4	100/15	15/1	1/2	2H	H	no blister	very good	good

TABLE 4

Composition No.	Primer formulation	Properties of coat			
		Pencil hardness	Brine spray test result (24 hrs)	Abrasion resistance	Adhesion strength (kg/cm)
		200°C			
1	No. 3 of Example 1	H	F	no blister	2.0
2	No. 4 of Example 1	2H	H	no blister	1.5
3	No. 6 of Example 1	HB	2B	no blister	0.9
4	No. 7 of Example 1	3H	2H	blistered	2.5

TABLE 5

Composition No	PPS/TiO ₂	Weight ratio PPS/PI	PPS+PI/ PTFE	Properties of coat			Repellency
				Room temp.	200°C	Brine spray test result (200 hrs)	
1	100/5	20/1	1/5	H	F	no blister	very good
2	100/5	20/1	1/3	H	F	no blister	very good
3	100/5	20/1	1/2	2H	F	no blister	very good
4	100/5	20/1	1/1	2H	F	no blister	very good
5	100/5	20/1	2/1	3H	H	no blister	good

Example

WHAT WE CLAIM IS:-

1. A coating composition comprising a polyarylene sulphide resin, a fluorocarbon polymer, and at least one imido-containing resin selected from polyamideimide resins and polyimide resins. 5

5 2. A coating composition according to Claim 1, wherein the fluorocarbon polymer content is from 5 to 1 parts by weight per one part by weight of the polyarylene sulphide resin and the imido-containing resin taken together. 10

10 3. A coating composition according to Claim 1, wherein the fluorocarbon polymer content is from 3 to 1/3 parts by weight per one part by weight of the polyarylene sulphide resin and the imido-containing resin taken together. 15

15 4. A coating composition according to any preceding claim, wherein the fluorocarbon polymer is selected from homopolymers and/or copolymers of tetrafluoroethylene. 20

5. A coating composition according to any preceding claim, wherein the weight ratio of the polyarylene sulphide resin to the imido-containing resin is in the range from 1:5 to 50:1. 15

6. A coating composition according to any preceding claim wherein the polyarylene sulphide resin is a polyphenylene sulphide resin. 25

7. An article having a fused coat of a coating composition according to Claim 2 or any claim appendent thereto. 30

8. An article having a fused coat of a coating composition according to Claim 3 or any claim appendent thereto, overlaid with a topcoat film of a fluorocarbon polymer. 20

9. A coating composition according to Claim 1 and substantially as hereinbefore described with reference to the Examples. 30

10. An article according to Claim 7 or Claim 8, and substantially as hereinbefore described with reference to the Examples. 25

25 11. An article whenever coated with a composition according to any of Claims 1 to 6 or 9. 25

LLOYD WISE, TREGEAR & CO.

Chartered Patent Agents.

30 Norman House,
105-109, Strand,
London, WC2R OAE. 30

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1981.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

THIS PAGE BLANK (USPTO)